DEVELOPMENT OF PHOTOCATALYTIC ACTIVE BUILDING MATERIALS USING ZNO NANORODS

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Abstract

In many urban cities, the pollutants concentration at street level is quite high because of the dispersion of the exhaust generated by a large number of vehicles is hindered by surrounding tall buildings. Control of these pollutions has become a pressing need for the well-being of society. Many methods have been developed to control these pollutions. Currently, there is an increasing interest in the control of urban pollution level by using construction materials containing photocatalytic nanomaterials, without changing original performance of the building structure. The photocatalytic materials used in the building materials for the purification process are efficient to remove the contaminants such as NO_x and VOC. Many works have been concerned with the application of different types of nanomaterials in photocatalytic processes. This paper presents the systematic study on the photocatalytic activity of ZnO nanorods on construction materials. In this method, ZnO nanorods were successfully synthesized by a wet chemical route. Systematic experiments were carried out to investigate the photocatalytic activity of the samples. The prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). It has been found that the ZnO nanoflowers contain many radial nanorods with the diameter of 100 nm and the length of 1–1.5 μm and these ZnO single-crystalline nanorods with wurtzite structure grow along the [0 0 1] direction. The formation mechanism of ZnO nanoflowers and nanorods was initially interpreted in terms of the general theory of the crystal nucleation and crystal growth direction. ZnO with flower-like morphology exhibited improved ability on the photocatalytic degradation.

Key Words: *ZnO, Photocatalysis, Construction, Nanomaterials, Nanotechnology*

1. Introduction

In the quest of making better materials for future, material engineers and scientists have not overlooked possibility of incorporating photocatalytic nanomaterials to construction materials [1]. These materials are especial class of semiconductors which inherit special property of forming radicals upon the irradiation with light at suitable wavelength, typically in the UV region. The process is best driven with the presence of moisture and oxygen gas, which can react with excited electrons and holes undergoing simultaneous oxidation and reduction [2]. Self cleaning coatings on material surfaces was realized with these materials, and currently gaining popularity in applications such as, self cleaning walls, floor and garden tiles, self cleaning glasses, self cleaning roofs etc [3]. The primary photocatalyst used in these applications is nano Titanium dioxide, which is appropriate for these applications because of its high photocatalytic activity, environmental stability, less toxicity etc [2, 4-6].

Although not very popular like TiO_2 in civil and environmental engineering applications, ZnO also carries very interesting properties as a photocatalytic material. The efficiency of ZnO as a photocatalyst increases with the increase of surface to volume ratio compared with bulk ZnO materials. The main advantage of ZnO over TiO_2 is relative ease of preparation of phoptocatalytic nanostructures. Number of simple as well as complex forms of ZnO nanostructures was reported in literature including, nanorods, nanobelts, nanotubes, nanorings and hierarchical structures [7]. On the other hand some of the above reported structures show superhydrophobicity due to high surface roughness. Development of building materials with both photocatalytic as well as superhydrophobic property may be of great interest in the future. Feng,[8] reported the switchable superhydrophobicity and superhydrophilicity of ZnO nanowire array films by alternating the UV irradiation.

ZnO nanorod arrays are relatively easily prepared and show high photocatalytic activity due to high surface area compared to ZnO nanoparticles mostly due to their high purity and crystallinity [9, 10]. In addition it's also reported that once the diameter of the nanowire or nanorod reduced below a critical value the effective bandgap of ZnO will increase and so does the redox potentials, therefore producing electron holes with higher reducing/oxidizing power. In nanorod structures, charge transfer efficiency between the catalyst and the pollutant is known to be high.

This is partly due to the increase of bandgap hinder the recombination of photo generated electron hole pares [11].

In this paper we suggest a procedure of preparation of ZnO nanorod arrays on glass substrate using a seed mediated growth process, to introduce photocatalytic activity to the material. Here we have characterized the nanorod arrays using different methods and photocatalytic activity of the ZnO nanorods for the degradation of synthetic stain Bromothymol blue was investigated.

2. Materials and methods

2.1. Materials

Zinc nitrate hexahydrate, Ammonia solution, Polyethylene glycol - Average Mn 4000 were purchased from Sigma-Aldrich. All chemicals were of analytical grade and used without further purification.

2.2. Deposition of ZnO seed layer films

The ZnO seed layer films were grown on a clean glass substrate by using a simple low-temperature successive ionic layer adsorption and reaction (SILAR) method. The properly cleaned glass substrates were used for entire experimental. $Zn(NO_3)_2$ was dissolved in diluted ammonia to get zinc ammonium complex solution ($[Zn(NH_3)_4]^{2+}$) which served as a cationic precursor. Distilled water kept at 80˚C was used as anionic precursor. The SILAR (Successive Ionic Layer Adsorption and Reaction) growth is a four step process involving subsequent immersion of glass substrate in cationic and anionic solution along with rinsing the substrate in between with water kept at room temperature. Initially, the substrate was immersed in $Zn(NO_3)_2$ and ammonia solution, where Zn^{2+} reacted with ammonia and formed zinc-ammonia complex. During the first immersion process, zinc ammonia was adsorbed on the glass substrate. This was immersed in distilled water, where the adsorbed zinc ammonia complex converted into zinc hydroxide ($Zn(OH)_2$). This was subjected to ultrasonic agitation to remove loosely bonded zinc hydroxide ($Zn(OH)_2$) molecules. Finally, the zinc hydroxide coated substrate was immersed into the distilled water bath at 80 ◦C, where $Zn(OH)_2$ was converted into solid ZnO film. The as-prepared ZnO seed layer films were subjected to annealing at 200◦C in steps for 1 h.

2.3. Preparation of hierarchical ZnO nanostructures thin films

First, 2g of $Zn(NO_3)_2$.6H2O was dissolved in 250ml of distilled water under stirring. The mixture of PEG (Mw=4000) and 3ml of ammonium hydroxide was added dropwise while the solution is stirring. The reaction mixture was heated rapidly to 70°C with vigorous stirring. The cotton fabrics coated with ZnO nanocrystals were immersed with in this solution, and it was sealed and allowed to grow nanorods over 24 h at 70°C. Then the cotton substrate was taken out and washed with distilled water and dried at 70°C for 20 min.

2.4. Photocatalytic experiment

Prepared ZnO nanorod grawn glass sample was stained with bromothymol blue having a concentration of 3 mg/L, prepared with 2% alcohol solution in water. Staining was done by placing a few drops of water on the sample and allows it to fully spread, and dry under room temperature under dark condition. The stained glass piece is irradiated by UV-A radiation using two UV-light mercury lamps (PHILLIPS TL-K) operating at the power rating of 40W. The surface of the sample was kept in a distance of 15 cm from the bulb. Diffuse reflectance spectra was recorded using Shimadzu UV-VIS-NIR UV-3600 spectrophotometer and kubelka-munk transform was performed to calculate the absorbance value of stain at different time intervals of UV exposure.

2.4. Instruments and characterization

The morphology of cotton samples were observed by a scanning electron microscope (SEM, su6600, operating at 30 kv). Structural characterization of ZnO nanorods were done by X-ray diffraction (XRD) using a Bruker D8 diffractometer (with Cu Kα = 40 kv), the UV-vis diffuse reflectance spectra were measured on SHIMADZU, UV-3600, UV-VIS-NIR, The photoluminescence (PL) spectra were recorded at room temperature using Flurolog (FL-1039 Horiba Jobinyvon) with excitation wave length of 350nm.

3. Results and Discussion

3.1 Morphology characterization

Scanning electron microscope was used to observe the morphology of ZnO rods grafted glass substrate at different magnifications. Fig 1 shows randomly distributed ZnO nanorods with hexagonal shaped morphology with a diameter of 100 to 250 nm. The variation in the diameter of the ZnO nanorods might be resulted from the non-uniform size distribution of ZnO seed layer. Top-view of SEM image reveals that the nanorods have perfect hexagonal shape.

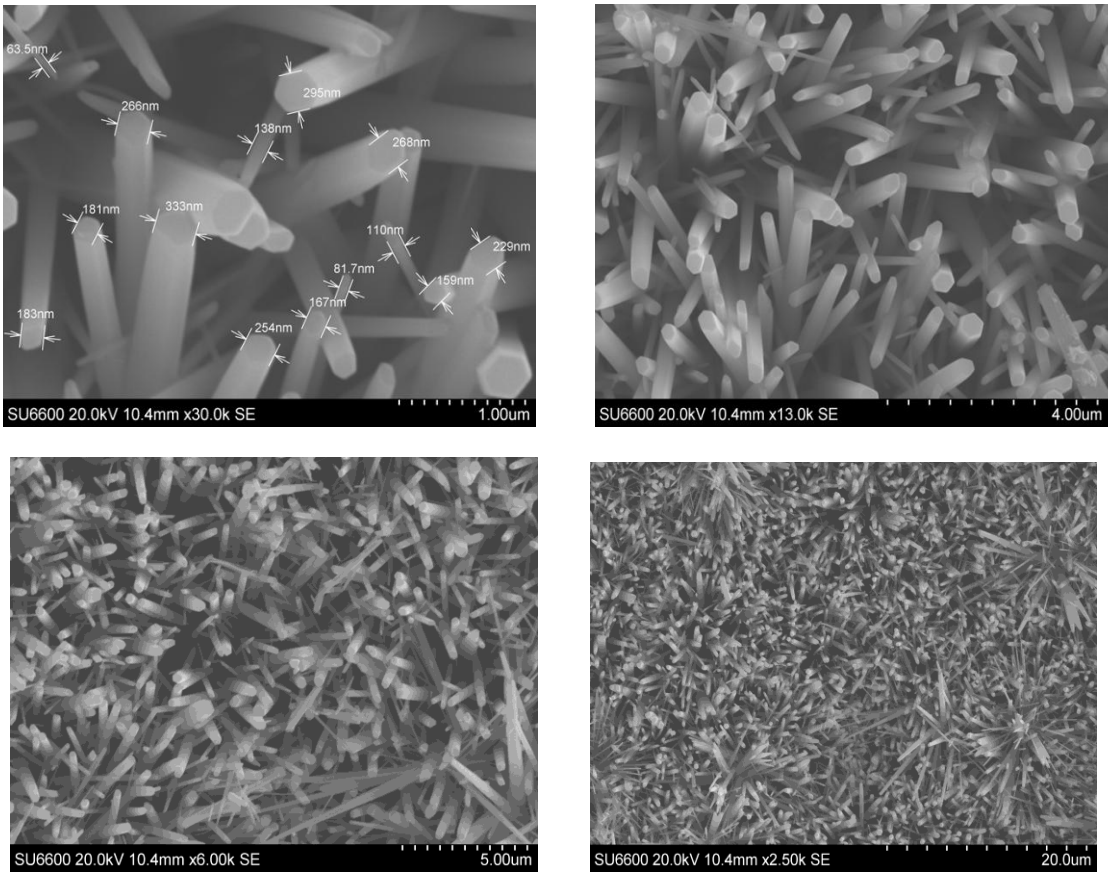

Figure 1: SEM images of ZnO nanorods on glass substrate

3.2. XRD spectrum Analysis

Fig. 2 shows XRD pattern of ZnO nanorods film grown on glass substrate. It shows a very sharp peak at 34.44◦ corresponding to (0 0 2) orientation of ZnO nanorods. The intensity of (0 0 2)

orientated peak is much higher intense than any other ZnO nanostructure peaks indicates that the CBD grown ZnO nanostructure film on annealed seed layer substrate. All other less intense peaks at 31.7◦, 36.16◦, 47.56◦ and 62.82◦ are corresponding to the (1 0 0), (1 0 1), (1 0 2) and (10 3) diffraction planes are corresponding to pure ZnO phase and there is no other peaks corresponding to intermediate $Zn(OH)_2$ or other residual impurities.

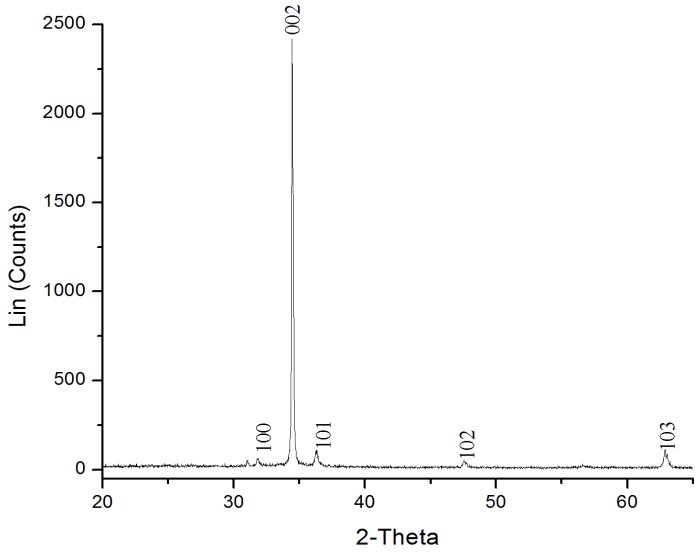

Figure 2: XRD spectrum of ZnO nanorods on glass substrate

3.3. Photoluminescence analysis

Fig. 3 shows the photoluminescence (PL) emission spectra from the ZnO NRs grown on a glass substrate. In general, an edge emission at 390 nm and a broad visible emission around 450–530 nm are observed in ZnO related nanostructures. The edge emission is due to the recombination of electrons from conduction band to valence band. However, this emission is mostly degraded by the surface defect states resulted from the large surface to volume ratio of nanostructures and as well as by other imperfections at the boundaries which usually resulted from the growth methods and conditions [14]. In our case, the emission at 390 nm is not resolved. The degradation in the emission at this wavelength is due to the presence of large defect states originated from both the size effect and as well as by our growth method. A peak at 560 nm was observed for our sample as shown in fig 3.

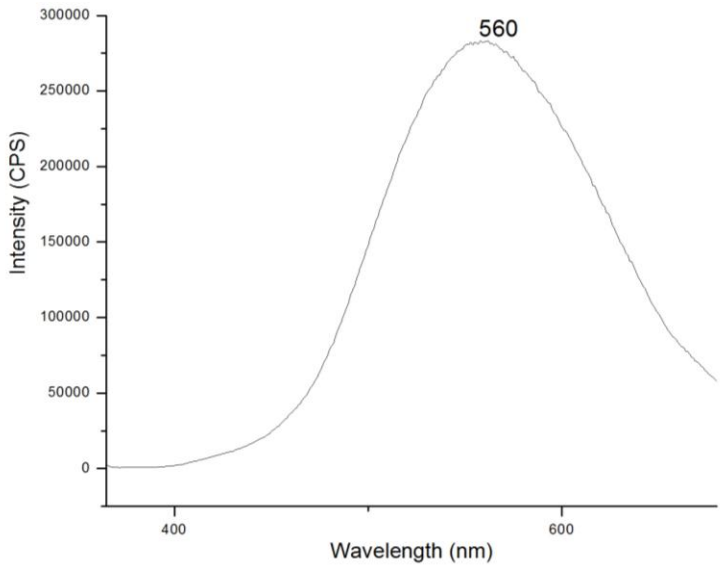

Figure 3: PL of ZnO nanorods on glass substrate

In order to evaluate the photocatalytic activity of ZnO nanorods grown on the glass substrate, photodegradation of bromothymol blue was investigated. The absorbance spectra of the stained glass at different time intervals of exposure are given in Figure 4.

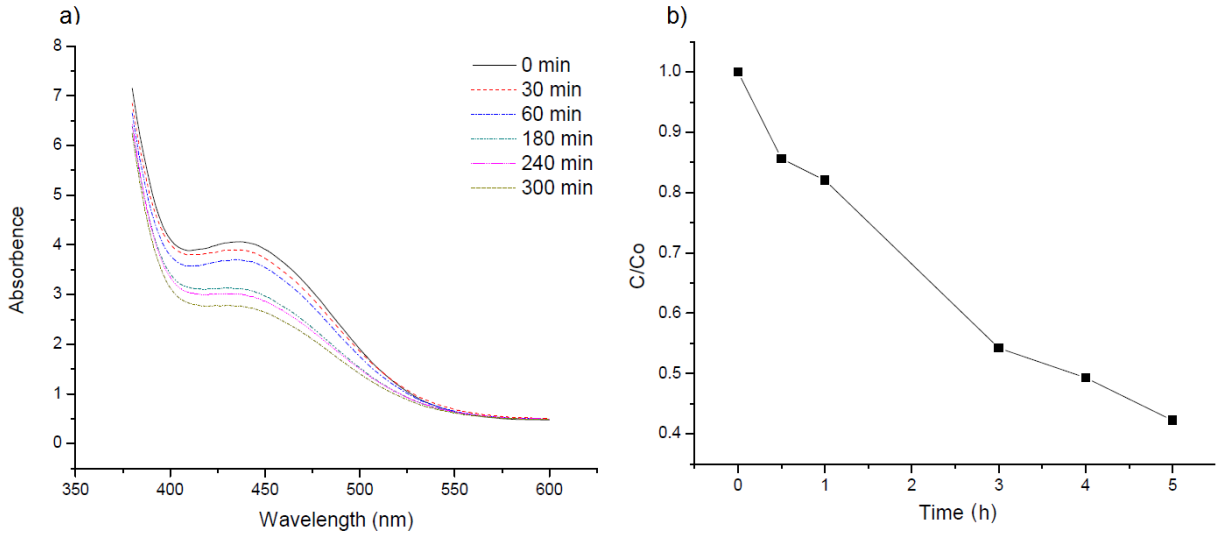

Figure 4: Photodegradation of bromothymol blue a) Absorption spectra of stained ZnO nanorod grown glass sample b) Linear degradation rate of bromothymol blue

The absorption of bromothymol blue showed a broad peak centered around ~470 nm and underwent an intensity decrease with UV light exposure time (Figure 4.a). In addition it could be seen that the nearly 60% solid state reduction of organic stain was achieved within 5 hours. The

mechanism that best represents heterogeneous photocatalytic degradation process was well investigated and discussed extensively in the literature [12]. When ZnO semiconductor absorbs a photon energy, that is greater than or equal to its band gap, an electron may be excited to conduction band leaving behind a hole or an electron vacancy. If the recombination does not occur instantaneously, some electrons and holes can migrate to the surface where they can participate with redox reactions with sorbed species such as organic pollutants.

Typically h+ vb may react with surface sorbed H_2O to produce hydroxyl radical while electron may react with ambient oxygen to generate superoxide radical. Both these radicals can attack organic stains such as bromothymol blue and finally degrade them to simple products like CO_2 and H_2O.

4. Conclusion

In summery, ZnO nanorod arrays were fabricated on glass slides to demonstrate the application of photocatalytic self cleaning building glass applications. The nanorods has diemeters in the range of 100 – 200 nm while maintaining perfect hexagonal plane on the end. The growth direction was confirmed to be (001) with XRD. Photocatalytic activity of the densly packed ZnO nanorod arrays were measured using visual diffuse reflectance, where approximately 60% of stain reduction was achieved withing 5 hours. These results, combined with inexpensive and relatively fracile method of preperation suggests glass/ZnO nanorod system is a promising material to be used in architecteral applications.

5. References

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